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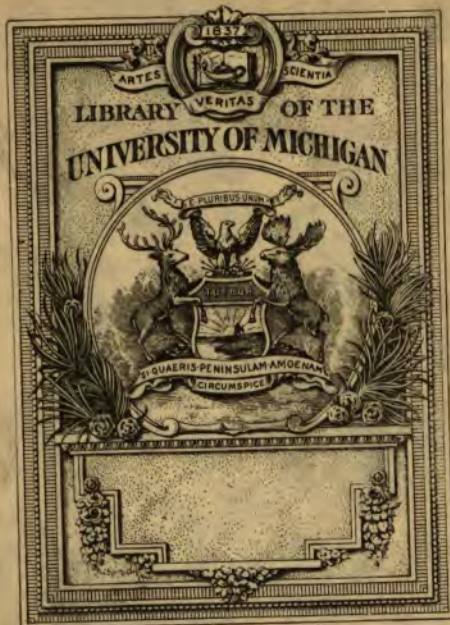
RESULTS OBTAINED
— IN —
ELECTRO-CHEMICAL ANALYSIS
BY THE USE
— OF A —
MERCURY CATHODE.

THESIS

PRESENTED TO THE FACULTY OF THE DEPARTMENT OF
PHILOSOPHY OF THE UNIVERSITY OF PENNSYLVANIA
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

— BY —
RALPH EMERSON MYERS, M. S.

AKRON, OHIO.



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INTRODUCTION.

It has been clearly demonstrated in recent years that valuable electrolytic determinations and separations of metals are possible with the aid of a mercury cathode.

Literature.—Gibbs, Chem. News, 42, 291; Gibbs, Am. Chem. J., 13, 571; Luckow, Ztschr. f. anal. Chem., 25, 113; Vortmann, Ber., 24, 2749; Drown and McKenna, J. anal. Chem., 5, 627; Smith, J. Am. Ch. Soc., 25, 883; Coehn and Kettembeil, Z. f. anorg. Ch., 38, 198; Kettembeil, Z. f. anorg. Ch., 38, 213.

The purpose of the present investigation was to extend this method to elements which had never been studied under such conditions. The results have been most satisfactory and are decidedly helpful to the analyst.

APPARATUS.

It seems advisable to describe the apparatus and the manner of using it. The decomposition cell used by Smith consists of a small beaker (50 cc. capacity), on the side of which, near the bottom is introduced a thin platinum wire. This wire is in contact internally with the mercury, which is introduced into the beaker, and externally with a copper plate, upon which the beaker is placed during electrolysis. The copper plate being connected with the negative electrode of a battery, the mercury becomes the cathode.

Considerable difficulty was experienced by the author, in the proper annealing of the beakers in which the wire was inserted, on or near the bottom curve. It was desirable to reduce the weight to a minimum, and as this could only be accomplished by having the wire placed directly on the curve, it became necessary to devise a modification of the above apparatus.

Construction of Cell.—The soft glass of a ten inch test tube is admirably suited to withstand the manipulation necessary to shape it into the desired form. The lower part of the test tube is warmed thoroughly in the smoky flame, and then the apex of a small blow pipe flame is applied at the point where it is desired to introduce the wire. The tube is blown out, care being taken to obtain a hole only slightly larger in diameter than the wire. The whole lower end of the tube is then reheated in the smoky flame; this reheating is repeated from time to time to prevent the formation of undesirable strains in the glass. The wire is then sealed in with the assistance of a small

globule of lead glass. The latter is first fused symmetrically onto the wire, the final seal being made with the fine blow-pipe flame. The standard or base of the cell is made as follows: The extreme lower end of the tube, that part below the platinum wire, is softened in the brush flame of the blast lamp and pressed down upon an asbestos card, the tube meanwhile being held in a vertical position. A flat bottom is not obtained, as the tube rolls into itself and produces an arched or dome-like surface, which is quite an advantage in that it occupies space which would otherwise be filled with the specifically heavier mercury. The cell is completed by cutting off the tube at the desired length and rounding up the rough edge so produced by softening the glass slightly in the flame. The best success in the cutting of the tube was achieved, by scratching with a file, a complete circle around the tube at the point where the cut was desired, and the subsequent application of the red hot point of a file to the scratch. The cell is annealed in the usual manner by wrapping in cotton. It was found that the decomposition cell, constructed in this manner, when filled with mercury to a level just above the platinum wire, affords the mercury surface required, and at a weight not exceeding 100 grams. Further the cell withstands without fracture the boiling temperature, which is frequently reached in the course of a decomposition.

Six cells of the above form were used in this investigation. They are of three sizes, which will be designated as Nos. 1, 2 and 3. The largest, No. 1, is 8.5 cm. tall and about 3.5 cm. in diameter. It holds 70 c. c. when filled to within 1.5 cm. of the top, and the upper surface of its mercury content, approximates closely to 10 sq. cm. in area. Cell No. 2 is 8 cm. by 3 cm.; it holds about 45 c. c. and has a mercury surface of 7 sq. cm. Cell No. 3 also has a mercury surface of 7 sq. cm., but holds only 35 c. c., as it is shorter, being only 6.5 cm. tall. It

is to be understood that these cells were used interchangeably in the work which is to follow, unless special mention is made to the contrary, as under chromium and molybdenum. Therefore, the dilution, except in special cases, is not an important factor, and may vary within wide limits. The beakers, Nos. 1, 2 and 3 weigh, respectively, 22, 26 and 20 grams; hence when filled so that the gross weight is between 95 and 100 grams, they contain anywhere from 70 to 80 grams of mercury.

Mercury.—The mercury need not necessarily be of special purity. That used in the following work was of the ordinary commercial variety, and was taken directly as it comes from the stoneware bottle, without redistillation.

Anode.—Platinum wire 1 mm. in diameter is bent in the usual spiral form to serve as an anode. The latter should be at least 1 cm. longer than the cell with which it is to be used.

Stand.—The usual electrolytic stand is used, a square of polished copper being placed upon the ring to serve as a base for the decomposition cell.

Source of Current.—Chloride accumulators (Type E) were used as the source of the electrical energy. Five cells connected in series was the usual arrangement, although at times eight or ten were used in special cases.

Instruments.—Three Weston instruments were available. The ammeter or the milliammeter, as the case might be, was kept in the circuit throughout the deposition. The ammeter, which was graduated to fifths, read to 25 amperes. The milliammeter which was graduated to hundredths, was capable of measuring currents up to one ampere. The voltmeter of 50 volt capacity, reading to one-half volt, gave the difference in potential between the electrodes of the decomposition cell. A rheostat of the usual form was present for the purpose of current regulation.

METHOD OF PROCEDURE.

In order to insure similar conditions in the weighing of the mercury, before and after the deposition, it is first washed with water, alcohol and ether, as described below, before the original tare is taken. As was mentioned, the amount of mercury taken is such that the gross weight does not exceed 100 grams, that amount being the carrying capacity of the balance used in this investigation. Watch crystals must be used to cover the cells when being carried to and from the balance room, as minute globules of mercury are readily detached, even by the motion produced in walking. Too much stress cannot be laid upon this point, and if due precaution is observed, the experimenter will not be troubled by losses, which seem unaccountable.

The solutions used were made up in considerable quantity from the purest salts obtainable. For analysis, a definite portion of the stock solution is removed by means of a pipette, the usual precautions being observed to insure uniformity in the operation. After the cell is placed on the stand, the proper dilution is made, and the sulphuric acid (Spg. 1.832—) necessary to produce the desired conductivity is added. The acid, when measured by drops, was dropped from a tube such that five drops equalled 0.2 of a c. c. The separation of the electrodes varied in the experiments following, between 1 and 2 cm. Variation within these limits produced no appreciable effect in the result. During the deposition the cell is provided with cover glasses, notched to allow the passage of the anode. These glasses can be readily made from the slides used in microscopic work. The cover glasses should be washed down from time to time, as also the walls of the beaker itself.

The time necessary for a deposition varies from five to twenty-four hours, depending on the amount of metal to be

deposited.¹ When the necessary time has elapsed for the deposition, the acid liquid remaining is siphoned off, distilled water being added as the level drops to the spiral of the anode. When the ammeter needle returns nearly to zero the washing is interrupted.

The washing and drying are accomplished as follows: The cell is filled one-third full with water and is rotated around its longitudinal axis after the latter has been tilted 45° to the vertical. By this means, the whole surface of the mercury as well as the whole inner surface of the cell is completely freed from the last traces of the electrolyte. This operation is repeated with two or three changes of water. Alcohol is then substituted for water, the first washing being discarded. The alcohol from the two remaining washings is returned to the stock bottle and is used again. The mercury is then treated three times with ether. Absolute alcohol and ether, though preferable, are not absolutely essential. It is sufficient to distil the alcohol over lime and the ether over anhydrous Calcium Chloride. When the ether becomes overcharged with water and alcohol, it shows a tendency to cause the mercury to separate into fine black shreds, which float off in the ether and thus occasion loss. This happens most frequently with mercury which is free from amalgam. The difficulty is removed by a distillation of the ether over Calcium Chloride. After five to ten minutes the odor of ether disappears from the cell. It is then cleaned externally by means of a cloth and the moisture from the breath. The final traces of ether and moisture are removed by allowing the cell to remain in a desiccator over sulphuric acid for a period of fifteen minutes. In order that the cell may come to the temperature of the balance case, it

¹When 14 hours is given as the time used for a deposition, the precipitation was made during the night, and really consumed only about four hours of the operator's time.

is allowed to remain for five minutes, on the balance pan, before the weighing is made.

Remarks.—The following experiment was made to determine what loss, if any, was suffered by the mercury while standing in the desiccator. A cell filled and prepared as above was weighed. It was then returned to the desiccator and reweighed at intervals of twenty-four hours. A loss of 0.0001 gram per day was observed during the first week. The rate of loss then decreased to such an extent that the total loss after a period of twenty-six days amounted to only 0.0015 gram. It was frequently found upon reweighing a cell in the morning that no loss had occurred, the cell having remained in the desiccator over night.

It is necessary to keep the inside of the cell absolutely clean, otherwise the amalgam shows a tendency to cling to the glass. Losses may occur from this source, as exceedingly small globules of mercury are often detached by the wash water, as well as the alcohol and ether.

When it is necessary, toward the end of certain decompositions, to neutralize a part of the acid present, this is best done by the addition of caustic potash in preference to ammonia. The latter causes the formation of trees of ammonium amalgam, which, in breaking down after the interruption of the current give off mercury in a very fine state of division. A cloudy wash water and consequently a low determination usually result.

As is demonstrated under the Separation of Iron from Beryllium and of Chromium from Aluminium, the element left in the wash water is in an excellent state for subsequent determination; the electrical reagent does not leave a filtrate surcharged with the excess of the precipitant.

EXPERIMENTAL PART.

DETERMINATION OF CHROMIUM.

Text books on electrochemical analysis make no mention of the estimation of the element chromium. It has never been determined electrolytically. When it was found that a solution of chromium sulphate slightly acidulated with sulphuric acid would yield its chromium to a mercury cathode, it was hoped that a method for the quantitative estimation of this element might be secured. Further investigation proved that this could be accomplished. A solution of chromium sulphate (Merck) containing 0.1080 gram of chromium per each 10 c. c., was used as the stock solution. Portions of this were pipetted off and electrolyzed. The conditions and results are given in Table I. The wash waters gave no evidence of the presence of chromium, even after concentration.

I. DETERMINATION OF CHROMIUM.

	Chromium present in grams	Chromium found in grams	No. of cell used	Sulphuric acid (Sp. g. 1.832) present in drops	Time Hours	Conditions			
						Amperes	Volts	Amperes	Volts
1.	0.1080	0.1079	2	2	3	0.3	7	0.55	5.5
2.	0.1080	0.1080	1	3	14	0.3	7	0.55	5.5
3.	0.2160	0.2157	1	4	14	0.4	7.5	0.7	6
4.	0.2160	0.2160	1	4	14	0.4	7.5	0.7	6
5.	0.3240	0.3235	1	8	30	0.7	7	2	6.5
6.	0.3240	0.3222*	1	6	30	0.65	7	2.5	8

* Some chromium floated off in wash water (see discussion).

The initial voltage and amperage is given to the left in the table. The acid liberated during the course of the electrolysis causes the potential to fall and the current to rise to the final

voltage and amperage, which is given to the right. On depositions run through the night, as all requiring over 12 hours were, the final current conditions were maintained for the last two hours, in order to remove the last traces of chromium. Chromium amalgam decomposes quite readily, especially in contact with water, metallic chromium appearing as a fine black powder on the surface of the mercury. Hence, it is advisable to wash the amalgam as rapidly as possible, and again a given portion of mercury should not be used for more than one decomposition. It is the hope of the author that this ready decomposability of chromium amalgam can be used in the preparation of chromium of a high degree of purity. All other metals liable to be present, being soluble in nitric acid. This point will receive further investigation.

Experiments 5 and 6 were added to the table to show that under favorable conditions 0.3 gram of chromium can be taken up by the 75 grams of mercury used in a cell of this size. Trouble is experienced, however, in washing an amalgam of this strength, the chromium appearing on the surface of the mercury before the necessary washing has taken place. The low result in Experiment 6 is due to loss of chromium in the wash water. It is neither desirable nor necessary to deposit more than 0.2 gram of chromium under these conditions, as an aliquot part of chromium solution in question can be taken. The appearance of oxide of chromium in the electrolyte indicates the presence of an insufficient amount of acid for the current used. In such a case a new decomposition is started, more acid or a lower current being used. As the water should be removed rapidly from the chromium amalgam, a fairly anhydrous alcohol is preferable with this element.

SEPARATION OF CHROMIUM FROM ALUMINIUM.

The separation of chromium from aluminium in a gravi-

metric way is not all that could be desired, and no electrolytic method whatsoever has been offered. Upon electrolyzing a solution containing a mixture of chromium and aluminium sulphates, the metallic chromium leaves the solution and is deposited as such in the mercury. The aluminium sulphate remains in the cell and is siphoned off in the wash water, and can be determined in the usual way. Thus both the chromium and the aluminium are weighed directly. The solution of chromium sulphate used was the same as in the Determination of Chromium. A stock solution of aluminium sulphate was prepared, containing 0.1421 gram of alumina per each 10 c. c. Portions of these solutions were pipetted off as usual and the sulphuric acid added as indicated in the table.,

The aluminium in the wash water from Depositions 1 and 2 was precipitated with ammonia and weighed as oxide, with the usual precautions. Further evidence, that the element left in the wash water can be determined, is given under the Separation of Iron from Beryllium.

The initial voltage and amperage are given to the left of the last column of Table II. The current strength is gradually increased as the decomposition progresses and is raised to the values, given to the right in the table, during the last hour or two. The precautions given under the Determination of Chromium, must also be observed here. That is, the amalgam should be washed rapidly with fairly anhydrous alcohol and ether, and no more than 0.2 gram of chromium should be deposited in a cell containing 75 grams of mercury. Reference to Table II. shows not only that chromium and aluminium can be separated when present in nearly equal quantities, but also when a preponderance of either one is present.

II. SEPARATION OF CHROMIUM FROM ALUMINIUM.

	Chromium present in grams	Chromium found in grams	Alumina present in grams	Alumina found in grams	No. of cell	Sulphuric acid (Spg. 1.832) present in drops	Time Hours	Conditions			
								Amperes	Volts	Amperes	Volts
1.	0.1080	0.1080	0.1421	0.1423	1	6	14	0.35	6	0.8	6.5
2.	0.1080	0.1081	0.1421	0.1426	2	4	14	0.3	6	0.8	6.5
3.	0.0108	0.0107	0.2842		1	6	2	0.3	5.5	0.7	7
4.	0.0108	0.0107	0.2842		3	5	1½	0.3	5.5	0.85	7.5
5.	0.2160	0.2162	0.0142		1	6	24	0.6	6	1.8	7.5
6.	0.2160	0.2158	0.0142		1	5	14	0.4	8	1	7.5

III. SEPARATION OF CHROMIUM FROM BERYLLIUM.

	Chromium present in grams	Chromium found in grams	Beryllium oxide present	No. of cell used	Sulphuric acid (Spg. 1.832) present in drops	Time Hours	Conditions			
							Amperes	Volts	Amperes	Volts
1.	0.1080	0.1079	0.0818	1	4	14	0.3	6	3.5	5
2.	0.1080	0.1078	0.0818	1	4	4.5	0.3	6	3.5	5

SEPARATION OF CHROMIUM FROM BERYLLIUM.

Chromium can also be separated from beryllium in an analogous manner, the sulphate of beryllium, yielding nothing to the cathode of mercury. The stock solution of beryllium sulphate contained 0.0818 gram of oxide per each 10 c. c., and was free from iron and other elements which would enter the mercury under the conditions existing during the electrolysis. As indicated by Table III, a wide variation in the time necessary for this separation, is permissible, without injury to the deposit. No deleterious effects are produced by the prolonged action of the current, even for a period of ten hours after the

metal is completely deposited. This statement is not restricted to this separation alone, but applies in general to all depositions made by the author, with the mercury cathode.

DETERMINATION OF MOLYBDENUM.

The element molybdenum is ordinarily precipitated by the current on the cathode as the black hydrated sesquioxide¹ from solutions of sodium molybdate acidulated with sulphuric acid. This hydrated sesquioxide cannot be dried and weighed as such, nor can concordant results be obtained by its ignition to the trioxide, owing to the volatility of the latter. It must be dissolved from the platinum dish in nitric acid and evaporated carefully to dryness. It is then weighed as MoO_3 . It was found that an aqueous solution of molybdenum trioxide, acidulated with sulphuric acid, when electrolyzed with a cathode of mercury, gave up its molybdenum completely, a brilliant white amalgam being formed. It thus becomes possible to weigh molybdenum directly, as a product of the electrolysis. Experimentation proved that a solution of sodium molybdate acidulated with sulphuric acid could be substituted for the aqueous solution of the trioxide, with like results. Accordingly, a stock solution of sodium molybdate was prepared containing 0.0950 gram of molybdenum per each 10 cc. Portions of this were electrolyzed with the results and under the conditions given in Table IV. The wash waters, after concentration, gave no test for molybdenum with potassium sulphocyanide, zinc and hydrochloric acid.

All depositions which could not be completed in seven or eight hours were run during the night with a current of about 1.5 amperes. The depositions do not require much attention, so the time of the analyst which is actually consumed is reduced far below that given in Table IV. It is not advisable to use a

¹ Exner, J. Am. Ch. S., 25, 896.

current of more than two amperes in the presence of this large amount of sulphuric acid, as the latter, under the influence of the heat which is developed, seems to exert a slight solvent action on the mercury cathode. As was mentioned earlier, the drops of sulphuric acid given in the table are of such size that five measure exactly 0.2 of a cc. in volume. As under the Determination of Chromium, the use of too high a current for the amount of acid present is attended by the formation of a lower oxide, which precipitates out, and ruins the decomposition, as the oxide appears to be insoluble in dilute acid.

SEPARATION OF MOLYBDENUM FROM VANADIUM.

Molybdenum and vanadium occur together in minerals, and as their gravimetric separation presents many difficulties, an electrolytic method would be welcome. A solution of sodium vanadate acidulated with sulphuric acid was electrolyzed; the vanadium was reduced to a brilliant blue, but no increase was observed in the weight of the mercury. A stock solution of sodium vanadate was then prepared, containing 0.1002 gram of vanadium to each 10 cc. Portions of this solution were removed by means of a pipette, as usual. The same sodium molybdate solution was used as under the Determination of Molybdenum. The conditions favorable for the separation of

IV. DETERMINATION OF MOLYBDENUM.

	Molybdenum present in grams	Molybdenum found in grams	No. of cell used	Sulphuric acid (Sp. 1.832) present in drops	Time Hours	Conditions			
						Amperes	Volts	Amperes	Volts
1.	0.0950	0.0950	3	13	14	1.2	6	1.6	6.5 (2 hrs.)
2.	0.0950	0.0946	3	13	22	1.2	6	1.6	6 (2 hrs.)
3.	0.1900	0.1906	2	30	18	1.6	5.5	*1.4	7 (4 hrs.)
4.	0.1900	0.1903	2	25	20	1.6	5.5	*1.4	7 (4 hrs.)

V. SEPARATION OF MOLYBDENUM FROM VANADIUM.

	Molybdenum present in grams	Molybdenum found in grams	Vanadium present in grams	No. of cell used	Sulphuric acid (Sp. gr. 1.832) present in drops	Time Hours	Conditions			
							Amperes	Volts	Amperes	Volts
1.	0.0950	0.0950	0.1002	2	20	20	1.6	6.5	1.5	5.5 (3 hrs.)
2.	0.0950	0.0940	0.1002	3	20	18	2	5	1	5 (3 hrs.)
3.	0.1900	0.1895	0.0100	2	30	18	1.6	4.5	*1.5	6 (3 hrs.)
4.	0.1900	0.1887	0.0100	2	30	20	1.4	4.5	†1.2	5.5 (3 hrs.)

* Neutralized with caustic potash to 15 drops of sulphuric acid and then run under final conditions for time given.

† Neutralized with caustic potash to 20 drops of sulphuric acid and then run under final conditions for time given.

molybdenum from vanadium are given in Table V. As indicated in Experiments Nos. 3 and 4 in Table IV., also in Experiments Nos. 3 and 4 in Table V., it was found best to neutralize, with potassium hydroxide, a portion of the sulphuric present after all the molybdenum has been deposited, but the last traces. Large amounts of the acid seem to exert a retarding influence on the last traces of molybdenum. On the other hand the neutralization must not be carried too far, as an oxide of vanadium appears at the anode, when insufficient acid is present. When the molybdenum is completely deposited the solution is blue and not green; this may serve as a signal for the interruption of the current. The reader will please note that values given in Table V. are for molybdenum and vanadium and not for their oxides. An attempt was made to show that the method was applicable when 0.0095 gram of molybdenum was present with 0.2 gram of vanadium, but after many trials the idea was abandoned, as a vanadium solution of this concentration seems to prevent the complete deposition of the molybdenum. The method would doubtless work with these proportions, provided that a decomposition cell of double the capacity

were used. But this is unnecessary, as dilution will bring about the desired result.

SEPARATION OF IRON FROM THE RARE EARTHS.

Wolcott Gibbs¹ in the year 1883 first deposited iron, using a mercury cathode. The decomposition of the iron salt was complete, as the presence of that metal could not be detected in the wash water.

Drown and McKenna² separated iron from aluminium and phosphoric acid. Smith³ in his paper on the Uses of a Mercury Cathode in Electrochemical Analysis described methods for the separation of iron from uranium, titanium, zirconium, and thorium. Following a suggestion given in the latter paper, experiments were undertaken to determine the possibility of a separation of iron from the rare earths. Preliminary trials disclosed the fact that the sulphates of the earths gave nothing to the mercury, when electrolyzed under conditions suitable for the deposition of iron. Accordingly a stock solution of ferrous sulphate (Baker and Adamson, C.P.) was prepared, one drop of sulphuric acid (Spg. 1.832) being added for each 10 cc. of the solution. The average of five volumetric determinations of the iron content of 10 cc. of this solution gave 0.1056 gram of metallic iron. The following results were obtained by electrolysis, using the mercury cathode: 0.1057 gram, 0.1055 gram, 0.1058 gram, 0.1057 gram, 0.1055 gram, 0.1056 gram, and 0.1055 gram of iron. The wash waters gave no tests for iron with sodium sulphide. The deposition of iron with a mercury cathode presents no difficulty whatever. The various cells, which have been previously described, were used interchangeably in the following separations. The dilution, therefore, is not an important factor. Wide variations in the current density

¹ Amer. Chem. J., 13, 571.

² J. Amer. Chem. S., 25, 888.

³ J. Anal. Ch., 5, 627.

produce no marked effect, except in the time necessary for the deposition. The iron amalgam washes easily and shows no tendency to throw off metal in a fine state of division as was observed with chromium amalgam. After weighing off a deposit of iron, it is unnecessary to replace the amalgam in the cell with pure mercury before starting a new deposition, as the same mercury can be used repeatedly for successive depositions.

The earths available for this work were cerium, lanthanum, praseodymium, neodymium and yttrium, most of which were prepared by Shapleigh of the Welsbach Company. Stock solutions of the sulphates were prepared, and sulphuric acid added where necessary to prevent the formation of basic salts.

A glance at the following tables will show that satisfactory separations of iron from each of the earths can be obtained. As no difficulties are encountered, and as the tables express all that is necessary for the successful application of the method, no further discussion is necessary.

VI. SEPARATION OF IRON FROM CERIUM.

	Iron present in grams	Iron found in grams	Cerium dioxide present in grams	Sulphuric acid (Sp. g. 1.832) present in drops	Time Hours	Conditions			
						Amperes	Volts	Amperes	Volts
1.	0.1056	0.1055	0.0635	8	14	0.8	6	1	5.5
2.	0.1056	0.1058	0.0635	8	14	0.8	6	1	5.5
3.	0.0105	0.0103	0.1905	20	6	0.6	4.5	1	5
4.	0.0105	0.0106	0.1905	20	6	0.6	4.5	1	5
5.	0.2112	0.2112	0.0064	3	14	0.4	8	0.8	6
6.	0.2112	0.2113	0.0064	3	14	0.5	8	1	7

VII. SEPARATION OF IRON FROM LANTHANUM.

	Iron present in grams	Iron found in grams	Sesquioxide of lanthanum present in grams	Sulphuric acid (Spg. 1.832) present in drops	Time Hours	Conditions			
						Amperes	Volts	Amperes	Volts
1.	0.1056	0.1057	0.0432	5	6	0.6	6.5	0.8	7
2.	0.1056	0.1053	0.0864	2	14	0.4	8	0.8	8
3.	0.0105	0.0103	0.1728	6	14	0.4	7.5	0.6	9
4.	0.0105	0.0101	0.1728	7	14	0.4	7.5	0.6	9
5.	0.2112	0.2116	0.0129	3	14	0.4	6	1.2	8
6.	0.2112	0.2112	0.0129	3	14	0.4	6	1.4	8

VIII. SEPARATION OF IRON FROM PRASEODYMIUM.

	Iron present in grams	Iron found, in grams	Oxide of praseodymium present in grams	Sulphuric acid (Spg. 1.832) present in drops	Time Hours	Conditions			
						Amperes	Volts	Amperes	Volts
1.	0.1056	0.1055	0.1200	5	5½	0.5	6.5	1	7
2.	0.1056	0.1056	0.1200	5	14	0.5	6	1.2	9.5
3.	0.0105	0.0104	0.2400	7	5	0.6	6	0.8	7
4.	0.0105	0.0105	0.2400	6	5	0.6	7	0.8	7.5
5.	0.2112	0.2113	0.0160	4	14	0.4	6	1.2	8
6.	0.2112	0.2104	0.0160	4	14	0.4	6	1.2	8

IX. SEPARATION OF IRON FROM NEODYMIUM.

	Iron present in grams	Iron found in grams	Oxide of neodymium present in grams	Sulphuric acid (Spg. 1.832) present in drops	Time Hours	Conditions			
						Amperes	Volts	Amperes	Volts
1.	0.1056	0.1056	0.1089	2	14	0.5	6	1	8
2.	0.1056	0.1056	0.1089	2	14	0.5	6	1	8
3.	0.0105	0.0102	0.2178	4	4½	0.6	9	0.8	9
4.	0.0105	0.0102	0.2178	4	14	0.5	7	0.9	8
5.	0.2112	0.2108	0.0145	3	14	0.4	6.5	1.2	7
6.	0.2112	0.2112	0.0145	3	14	0.4	6.5	1.2	7

X. SEPARATION OF IRON FROM YTTRIUM.

	Iron present in grams	Iron found in grams	Yttria present in grams	Sulphuric acid (Sp. 1.832) present in drops	Time Hours	Conditions			
						Amperes	Volts	Amperes	Volts
1.	0.1056	0.1054	0.0320	6	14	0.5	6	0.8	7
2.	0.1056	0.1056	0.0320	6	6	0.6	6.5	0.8	7
3.	0.0105	0.0105	0.1280	10	6	0.6	6	0.8	6
4.	0.0105	0.0104	0.2080	12	4½	0.8	6	1.2	7
5.	0.2112	0.2112	0.0032	3	14	0.4	7	1	6
6.	0.2112	0.2111	0.0032	3	14	0.4	7	1	6

SEPARATION OF IRON FROM VANADIUM.

Knowing that iron enters the mercury and that vanadium does not, it was quite probable that a separation of iron from vanadium could be obtained.

The results given in Table XI. show this to be the case. The same difficulty was encountered here as under the Separation of Molybdenum from Vanadium, when 0.2 gram of vanadium was present. Just as 0.2 gram of vanadium prevented the complete deposition of a small amount of molybdenum, so here it prevents the complete deposition of 0.0105 gram of iron. As suggested under molybdenum the use of a larger cell or the division of the solution will overcome the difficulty.

XI. SEPARATION OF IRON FROM VANADIUM.

	Iron present in grams	Iron found in grams	Vanadium present in grams	Sulphuric acid (Sp. 1.832) present in drops	Time Hours	Conditions			
						Amperes	Volts	Amperes	Volts
1.	0.1056	0.1054	0.1002	12	17	0.4	7	1	8.5
2.	0.1056	0.1051	0.1002	13	14	0.6	7	1	9
3.	0.2112	0.2113	0.0200	5	14	0.3	7	1	7.5
4.	0.2112	0.2112	0.0200	5	14	0.4	7	1	7

SEPARATION OF IRON FROM BERYLLIUM.

From the fact that chromium can be separated from beryllium there was every reason to suppose that iron could be separated from beryllium also. The preparation of the chromium sulphate and beryllium sulphate solutions has been described. As shown by Table XII., the results were highly satisfactory. For the purpose of further demonstrating that the element remaining in the wash water is in a suitable condition to be estimated, ammonia was added in each case and the beryllium hydroxide ignited to oxide and weighed. The results given are not selected results, but are consecutive determinations.

SEPARATION OF IRON FROM ALUMINIUM.

Drown and McKenna's separation of iron from aluminium was confirmed by a number of experiments. In the opinion of the writer this is the best separation of iron and aluminium extant.

XII. SEPARATION OF IRON FROM BERYLLIUM.

	Iron present in grams	Iron found in grams	Beryllium oxide present in grams	Beryllium oxide found in grams	Sulphuric acid (SpG. 1.832) present in drops	Time Hours	Conditions		
							Volts	Amperes	Volts
1.	0.1056	0.1057	0.0818	0.0821	2	7	0.5	7	0.8 6.5
2.	0.1056	0.1059	0.0818	0.0820	2	14	0.5	7	0.8 6.5
3.	0.0105	0.0105	0.1636	0.1633	2	4½	0.6	8	0.8 8
4.	0.0210	0.0208	0.1636	0.1630	2	14	0.6	8	0.8 8
5.	0.2112	0.2113	0.0082	0.0082	2	14	0.4	6.5	1.2 7
6.	0.2112	0.2112	0.0082	0.0083	2	14	0.4	6.5	1.2 7

RÉSUMÉ.

The results of this investigation may be summed up as follows:

